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Active Intermediates in Ethylene Polymerization over Titanium Bis(phenoxyimine) Catalysts

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Reactive intermediates in living olefin polymerization over homogeneous catalysts based on bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (L_2TiCl_2) have been studied. Outer sphere ion pairs $[L_2TiMe(S)]^+[Me\text{-}MAO]^-$ and $[L_2TiMe(S)]^+[B(C_6F_5)_4]^-$ (S = solvent molecule), formed by activation of L_2TiCl_2 with MAO or with $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$, and reactions of these ion pairs with ethene to afford chain-propagating species $[L_2TiP]^+[Me\text{-}MAO]^-$ and $[L_2TiP]^+[B(C_6F_5)_4]^-$ (P = growing polymeryl chain) have been characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.

Introduction

In recent years, olefin polymerizations with fluorinated bis(phenoxyimine) zirconium and titanium catalysts, discovered by Fujita,[1−5] have attracted considerable interest, especially with regard to their living nature.[6−15] These catalysts must be activated by Lewis acidic cocatalysts such as methylaluminoxane (MAO) and $AlR_3/[CPh_3]^+[B(C_6F_5)_4]^-$. While they show very high activity, their thermal stability is lower than that of metallocenes. In a recent study on the structure of active species in bis(phenoxyimine) titanium-based catalyst systems by ^{1}H NMR spectroscopy, Makio and Fujita observed the formation of two complexes, **A** and **B**, upon activation of bis[*N*-3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**1**) with MAO (Al:Zr = 100).[13] The ^{1}H NMR resonances of the initially formed species **A** were ascribed to a cationic species L_2TiMe^+, while the subsequently formed, inactive species **B** was proposed to be an aluminum complex $LAlMe_2$.

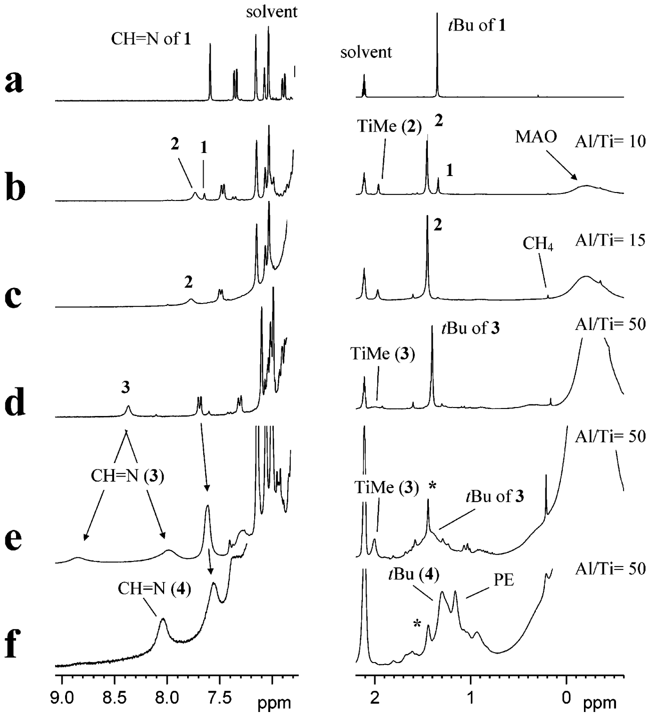

Figure 1. ^{1}H NMR spectra of **1** (a) and **1**/MAO samples (b−f): Al:Ti =10, 20 °C (b); Al:Ti =15, 20 °C (c); Al:Ti = 50, 20 °C (d); Al:Ti = 50, −20 °C (e); sample in e after addition of 20 equiv of ethylene at −20 °C (f) ([**1**] = 2.5 × 10^{-2} M, toluene-d_8). Asterisks mark *t*Bu signals of the deactivation product $LAlMe_2$.

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(1) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Tanaka, H.; Fujita, T. *Chem. Lett.* **1999**, 1263.

(2) Matsui, S.; Mitani, M.; Saito, J.; Tohi, Y.; Makio, H.; Matsukawa, N.; Takagi, Y.; Tsuru, K.; Nitabaru, M.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2001**, *123*, 6847.

(3) Matsui, S.; Fujita, T. *Catal. Today* **2001**, *66*, 63.

(4) Saito, J.; Mitani, M.; Mohri, J.; Yoshida, Y.; Matsui, S.; Ishii, S.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2918.

(5) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327.

(6) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev*. **2003**, *103*, 283.

(7) Mitani, M.; Nakano, T., Fujita, T. *Chem. Eur. J.* **2003**, *9*, 2396.

(8) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706.

(9) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626.

(10) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134.

(11) Pennington, D. A.; Clegg, W.; Coles, S. J.; Harrington, R. W.; Hursthouse, M. B.; Hughes, D. L.; Light, M. E.; Schormann, M.; Bochmann, M.; Lancaster, S. J. *Dalton Trans.* **2005**, 561.

(12) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res.* **2004**, *37*, 231.

(13) Makio, H.; Fujita, T. *Macromol. Symp.* **2004**, *213*, 221.

(14) Saito, J.; Tohi, Y.; Matsukawa, N.; Mitani, M.; Fujita, T. *Macromolecules* **2005**, *38*, 4955.

(15) Furuyama, R.; Mitani, M.; Mohri, J.; Mori, R.; Tanaka, H.; Fujita, T. *Macromolecules* **2005**, *38*, 1546.

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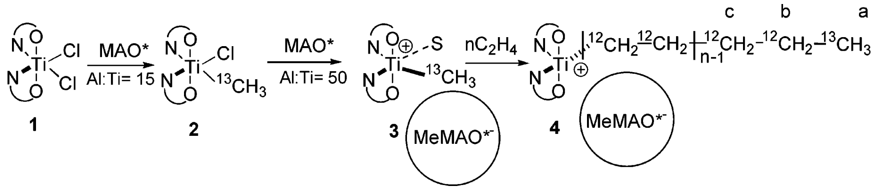
Table 1. Selected ^{13}C and ^{1}H NMR Chemical Shifts (ppm), Line Widths $\Delta\nu_{1/2}$ (Hz), and $^{1}J_{CH}$ Coupling Constants (Hz) for Complexes 1−4 and Reference Complexes in Toluene-d_8/1,2-Difluorobenzene[a]

species	Al:Ti	T, °C	^{1}H (N=CH)	^{13}C (Ti−Me)	^{1}H (Ti−Me)	^{13}C (tBu)	^{1}H (tBu)
L_2TiCl_2 (**1**)		20	7.56				1.35
$L_2TiClMe$ (**2**)	15	20	7.74 ($\Delta\nu_{1/2}$= 25)	79.3 [b]($\Delta\nu_{1/2}$ = 40)	1.97 ($\Delta\nu_{1/2}$ = 7)	29.3	1.46
$L_2TiClMe$ (**2**)	15	−40	7.55; 7.34		ca. 2.1[c]		1.53; 1.46
$[L_2TiMe(S)]^+$ $MeMAO^-$ (**3**)	50	20	8.32 ($\Delta\nu_{1/2}$ = 13)		2.00 ($\Delta\nu_{1/2}$ = 30)		1.40
$[L_2TiMe(S)]^+$ $MeMAO^-$ (**3**)	50	−20	8.81; 7.90	87.2 ($\Delta\nu_{1/2}$ = 42)[d] (J^{1}_{CH} = 127)	2.0 ($\Delta\nu_{1/2}$ = 14)	29.5	1.4 ($\Delta\nu_{1/2}$ = 40)
$[L_2TiP]^+$ $MeMAO^-$ (**4**)	50	−20	8.10 ($\Delta\nu_{1/2}$ = 35)				1.29[e]
$[L_2TiMe(S)]^+$ $[B(C_6F_5)_4]^-$ (**3′**)	25	20	8.38 ($\Delta\nu_{1/2}$ = 10)		2.01 ($\Delta\nu_{1/2}$ = 8)		1.35
$[L_2TiMe(S)]^+$ $[B(C_6F_5)_4]^-$ (**3′**)	25	−20	8.76; 7.91		1.95	29.1	1.4
$[L_2TiP]^+$ $[B(C_6F_5)_4]^-$ (**4′**)	25	−20	8.10 ($\Delta\nu_{1/2}$ = 35)				1.23[f]
$LAlMe_2$	50	20	7.38				1.46

[a] Ionic species **3** and **4** have limited solubility in toluene-d_8 and tend to form oily precipitates in the bottom of the NMR tubes. To increase the solubility of ionic species **3** and **4**, 10 vol % of 1,2-difluorobenzene was added. This did not affect dramatically the NMR patterns and the observed equilibria. [b] At −2 °C. [c] Overlapped with residual peak of toluene-d_8. [d] $\Delta\nu_{1/2}$= 270 Hz at −2 °C. [e] ^{13}C: 14.6 ppm ($H_3{}^{13}C$-$(CH_2)_n$-Ti), 23.4 ppm (d, $^{1}J_{CC}$ = 34.8 Hz, $H_3{}^{12}C$-$H_2{}^{13}C$-$H_2{}^{13}C$-$(CH_2)_n$-$H_2{}^{13}C$-Ti), 32.6 ppm ($H_3{}^{12}C$-$H_2{}^{13}C$-$H_2{}^{13}C$-$(CH_2)_n$-$H_2{}^{13}C$-Ti), 111.5 ($H_3{}^{12}C$-$H_2{}^{13}C$-$H_2{}^{13}C$-$(CH_2)_n$-$H_2{}^{13}C$-Ti), ^{1}H: 1.16 ($H_3{}^{13}C$-$(CH_2)_n$-Ti). [f] ^{1}H polyethylene peak at 1.11 ppm.

Scheme 1. Formation of Cationic Titanium-Polymeryl Species 4 (MAO* = ^{13}C-labeled MAO)



In this work, we report results of a detailed study of the interaction of **1** with MAO and with $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$ by ^{1}H, ^{13}C, and ^{19}F NMR and EPR spectroscopy, which provide further evidence for structures and reaction pathways of relevant intermediates in these catalyst systems.

Results and Discussion

The System 1/MAO. The ^{1}H NMR spectrum of the initial complex **1** in toluene-d_8/1,2-difluorobenzene (9:1) at 20 °C displays sharp and well-resolved peaks (Figure 1a, Table 1). After addition of MAO (Al:Ti = 15), the major part of **1** is converted to another complex identified as $L_2TiMeCl$ (**2**) (Figure 1b,c, Table 1). At 20 °C, the imine resonance of **2** is a broadened singlet (δ 7.70 ppm), indicating time-averaged C_2 symmetry. At −40 °C, it decoalesces into two peaks at δ 7.55 and 7.34, in agreement with the expected nonequivalence of two phenoxyimine ligands. An experiment with ^{13}C-enriched MAO revealed the expected Ti-$^{13}CH_3$ resonance at δ 79.3 ($\Delta\nu_{1/2}$ = 40 Hz, see Table 1).

At Al:Ti ratios of 20−30, the new complex **3** is present in the **1**/MAO system, together with complex **2**. The ^{1}H NMR spectrum of this sample at 20 °C corresponds to an exchange between complexes **2** and **3**, which is rapid on the NMR time scale, while at lower temperatures (< −20 °C) the ^{1}H NMR resonances of the imine protons of **3** and **2** can be observed separately (Table 1).

When the Al:Ti ratio is increased to 50, the starting complex **1** is quantitatively converted to complex **3** (Figure 1d, Table 1), which corresponds to complex **A** found by Makio and Fujita.[13] According to our results, it dominates in the reaction system under conditions approaching those of real polymerizations, at Al:Ti ratios of 50−500. At room temperature, the imine peak of **3** is observed at δ 8.32. At decreased temperatures it decoalesces into two signals of 1:1 ratio (δ 8.81 and 7.90 at −20 °C; Figure 1e, Table 1). This nonequivalence of the two phenoxyimine ligands of **3** indicates that two different ligands occupy the additional coordination sites of this complex. The estimated apparent $\Delta G^{\ddagger}_{ex}$ value of 12.5 kcal mol^{-1} (at coalescence temperature of −5 °C) is close to values observed for similar exchange processes in several alkyl-metallocene cations.[16]

Upon use of a ^{13}C-enriched sample of MAO, the ^{13}C NMR spectrum of **3** exhibits an intense Ti-Me peak at δ 87.2 ($\Delta\nu_{1/2}$ = 42 Hz, −20 °C, in toluene-d_8/1,2-difluorobenzene). Two-dimensional ^{13}C−^{1}H correlation revealed that this peak correlates with the ^{1}H NMR resonance at δ 2.0. The $^{1}J_{CH}$ value of 127 Hz determined for the resonance at 87.2 ppm corresponds to that of a terminal Ti-Me group (for a bridging Ti-Me-Al group, $^{1}J_{CH}$ values of 113−118 Hz would be expected[17]). These data and the downfield shift of the Ti-Me ^{13}C resonance of **3** (δ 87.2) from that in $L_2TiMeCl$ (δ 79.3) corroborate the assignment of **3** (i.e., of Makio and Fujita's complex **A**) to a cationic titanium species containing a terminal Ti-Me ligand.[17] The relatively sharp ^{1}H and ^{13}C NMR peaks of **3** indicate that the $[Me\text{-}MAO]^-$ counterion is placed in the outer coordination sphere of titanium.

For all inner-sphere ion pairs of the type $L'_2\mathbf{M}Me^+ \leftarrow Me\text{-}MAO^-$ (L'_2M = metallocenes,[18−20] half-titanocenes,[21] constrained geometry complexes;[17] with

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(16) (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Beswick, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10358. (c) Song, F.; Lancaster, S. J.; Cannon, R. D.; Schormann, M.; Humphrey, S. M.; Zuccaccia, C.; Macchioni, A.; Bochmann, M. *Organometallics* **2005**, *24*, 1315. (d) Beck, S.; Lieber, S.; Scharper, F.; Geyer, A.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2001**, *123,* 1483.

(17) Bryliakov, K. P.; Talsi, E. P.; Bochmann, M. *Organometallics* **2004**, *23*, 149.

(18) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A., Talsi, E. P. *Macromol. Chem. Phys.* **2000**, 201, 558.

(19) Bryliakov, K. P.; Semikolenova, N. V.; Yudaev, D. V.; Zakharov, V. A.; Brintzinger, H.-H.; Ystenes, M.; Rytter, E.; Talsi E. P. *J. Organomet. Chem.* **2003**, *683*, 92.

(20) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1997**, *30*, 1247.

(21) Bryliakov, K. P.; Semikolenova, N. V.; Zakharov, V. A.; Talsi E. P. *J. Organomet. Chem.* **2003**, *683*, 23.

M = Zr, Ti) strongly broadened NMR peaks have been observed, due to the nonuniformity of the tightly bound oligomeric [Me-MAO]$^-$ anions. The remaining coordination site of **3** is thus probably occupied by a weakly coordinated solvent molecule S, such that the interaction of **1** with MAO at high Al:Ti ratios would result in the quantitative formation of an outer-sphere ion pair, $[L_2TiMe(S)]^+[Me\text{-}MAO]^-$ (**3**).

In contrast to this, reactions of metallocenes with MAO (Al:**M** > 500) or $AlMe_3/[CPh_3]^+[B(C_6F_5)_4]^-$ generally afford heterobinuclear ion pairs of the type $[L'_2\mathbf{M}(\mu\text{-}Me)_2AlMe_2]^+[Me\text{-}MAO]^-$ (**III**) or $[L'_2\mathbf{M}(\mu\text{-}Me)_2AlMe_2]^+[B(C_6F_5)_4]^-$ (**III′**),[17–20,22,23] except for the sterically shielded complex *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}Bu\text{-}C_5H_2)_2ZrMe_2$, which interacts with Al_2Me_6 and $[PhNMe_2H][B(C_6F_5)_4]$ to afford an unsymmetrical ternary adduct *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}t\text{-}Bu\text{-}C_5H_2)_2ZrMe(\mu\text{-}Me)AlMe_2\text{-}NMe_2Ph^+$.[24] In this case, the bulky *tert*-butyl substituents prevent formation of a symmetric heterobinuclear ion pair of type **III.** In a similar manner, the bulky phenoxyimine ligands of **1** appear to prevent the formation of a heterobinuclear ion pair.

Ion pairs **3** formed in the catalytic systems **1**/MAO are unstable at room temperature and decompose via two main channels: (i) ligand transfer to aluminum with the formation of complex $LAlMe_2$ and (ii) reduction of titanium(IV) to titanium(III). The half-decay time of **3** in the sample **1**/MAO ([**1**] = 0.02 M, Al:Ti = 50, toluene-d_8, 20 °C) is about 1 h. The ^1H NMR spectrum of this species formed via decay of complex **3** in the **1**/MAO system (complex **B** reported by Makio and Fujita) coincides entirely with the previously reported ^1H NMR spectrum of $LAlMe_2$.[25] Comparison of the integral intensities of the ^1H NMR peaks shows that only a small part (<30%) of **3** is converted to $LAlMe_2$, while the major part of **3** transforms into some titanium(III) species unobservable by ^1H NMR. EPR spectroscopic data confirm the formation of a titanium(III) species during the decay of **3** in the **1**/MAO system.[26] For similar zirconium-based phenoxyimine catalysts, reduction of Zr(IV) to Zr(III) is less probable, and ligand transfer to aluminum is thus likely to be the main channel of catalyst deactivation.

The system **1**/MAO is a living catalyst for the polymerization of ethylene and propylene.[4] Addition of ethylene (20 equiv with respect to Ti) to the sample **1**/MAO (Al:Zr = 25) at −20 °C leads to immediate disappearance of the imine signals of **3**, while those of **2** ($L_2TiMeCl$) remain unchanged. While no residual ethene signal is observed in this reaction system, a new signal at δ 1.11 indicates the formation of a polyethenyl species.

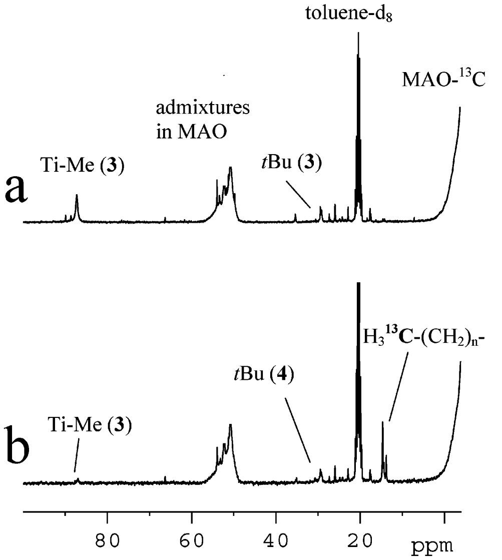

Figure 2. ^{13}C NMR spectra of **1**/MAO-^{13}C system before (a) and after (b) addition of 20 equiv of ethylene at −20 °C ([**1**] = 2.5 × 10^{-2} M, Al:Zr = 50, in toluene-d_8).

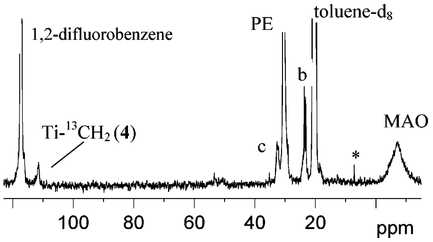

Figure 3. ^{13}C NMR spectrum of titanium-polymeryl species formed in **1**/MAO system after addition of 16 equiv of ethylene-$^{13}C_2$ at −20 °C ([**1**] = 2.5 × 10^{-2} M, Al:Zr = 50, toluene-d_8). Asterisk marks an admixture of $^{13}C_2H_6$. For notations b and c see Scheme 2.

This assignment is supported by the observation that the Ti-$^{13}CH_3$ NMR peak at δ 87.2, due to complex **3** formed in **1**/^{13}C-MAO (Al:Zr = 50), disappears upon addition of 20 equiv of ethene at −20 °C, concomitant with the appearance of isotopically enriched $^{13}CH_3$ polymeryl end groups at δ 14.6 (Figures 2a and 2b, Scheme 1). This shows unambiguously that complex **3** is the active species with regard to polymerization.

The ion pair $[L_2TiP]^+[Me\text{-}MAO]^-$ (**4**, with P = polymeryl chain), formed after addition of ethene at −20 °C, shows only one imine ^1H NMR peak at δ 8.10, instead of the two imine peaks of **3** at δ 8.81 and 7.90 (Figure 1f). In contrast to **3**, complex **4** thus contains equivalent phenoxyimine ligands even at −20 °C. Any additional ligand S, which might cause the reduced symmetry of **3**, is apparently lost when the methyl group of **3** is converted to a more bulky polymeryl chain in the propagating species **4**. Relatively sharp ^1H and ^{13}C NMR peaks of **4** indicate that the [Me-MAO]$^-$ counterion is placed in the outer coordination sphere of titanium. The remaining coordination site of **4** could be vacant or weakly coordinated by a polymeryl chain.

At room temperature, complex **4** decomposes, even faster than complex **3**, under formation of multiple unidentified signals.[27] To put the structural assignments of complexes **3** and **4** on a more reliable basis,

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(22) Bryliakov, K. P.; Babushkin, D. E.; Talsi, E. P.; Voskoboynikov, A. Z.; Gritzo, H.; Shröder, L.; Damrau, H.-R.; Wieser, U.; Schaper, F.; Brintzinger, H.-H. *Organometallics*, **2005**, *24*, 894.

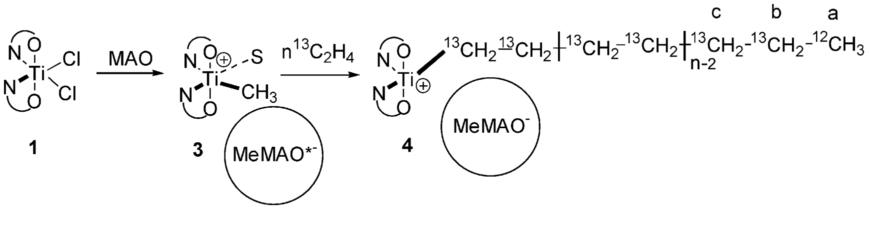
(23) Bochmann, M.; Lancaster S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(24) Schröder, L.; Brintzinger, H.-H.; Babushkin, D. E.; Fisher, D.; Mülhaupt, R. *Organometallics* **2005**, *24*, 867.

(25) Pappalardo, D.; Tedesco, C., Pellecchia, C. *Eur. J. Inorg. Chem.* **2002**, 621.

(26) EPR spectra of the samples L_2TiCl_2 + MAO (recorded after the decay of Ti(IV) species was confirmed by NMR) showed broad anisotropic signals, thus indicating the restricted tumbling of Ti(III) species probably due to coordination to bulky MAO molecules. The g_{iso} values of 1.977−1.978 are close to those measured for Ti(III) species observed in *ansa*-titanocene/MAO systems.[22] In the EPR spectra of the system L_2TiCl_2 + MAO + ethylene, two isotropic signals of Ti(III) were observed at g = 1.974 (minor) and g = 1.961 (major).

Scheme 2. Formation of the Cationic Titanium-Polymeryl-^{13}C Species 4



we have undertaken further studies with a perfluorophenyl borate activator and with ^{13}C-labeled ethene monomer.

The System 1/AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$. The ^{1}H, ^{13}C, and ^{19}F spectra of a sample of **1**/AlMe$_3$/[CPh$_3$]$^+$-[B(C$_6$F$_5$)$_4$]$^-$ = 1:10:1.1 ([**1**] = 0.04 M), prepared as described in the Experimental Section, show that the reaction of **1** with AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ at room temperature affords mainly the ion pair [L$_2$TiMe(S)]$^+$-[B(C$_6$F$_5$)$_4$]$^-$ (**3′**). The ^{1}H NMR spectrum of **3′** is very similar to that of **3**; as in **3**, the imine peak of **3′** decoalesces into two signals upon decreasing the temperature (Table 1). The ^{19}F spectrum of **3′** is typical for outer-sphere perfluoroarylborate anion [B(C$_6$F$_5$)$_4$]$^-$ (^{19}F, 20 °C: δ −132.4, −162.8, −166.7),[28–30] thus confirming the ion pair structure of **3′** and **3**. Apparently the trytyl cation abstracts the Me anion from L$_2$TiClMe to afford L$_2$TiCl$^+$ and then L$_2$TiCl$^+$ rapidly converts into L$_2$TiMe$^+$ upon interaction with TMA.

In the absence of monomer, complex **3′** is thermally unstable and decomposes at room temperature with a half-life of 2−3 h to form LAlMe$_2$ along with unidentified Ti(III) and Ti(IV) species. When ion pair **3′** reacts with ethylene, the resulting ^{1}H NMR signals in the imine, *tert*-butyl, and polyethenyl regions are closely similar to those previously observed for **4** (Table 1). This documents the formation of an outer-sphere polymeryl ion pair [L$_2$TiP]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**4′**) in this reaction system.

In Situ Polymerization of ^{13}C$_2$H$_4$ with 1/MAO. Polymerization of ^{13}C-enriched monomer in combination with NMR spectroscopy has previously been used to detect polymerizing species, mostly in titanocene[31a−d] and zirconocene[31e] based systems. To provide direct insights with regard to the role of cationic species **3**, ^{13}C$_2$H$_4$ polymerization was performed in the NMR tube and followed by ^{1}H and ^{13}C NMR at −20 °C. After injection of monomer (^{13}C$_2$H$_4$/Ti = 16) into a tube containing **3** ([**3**] = 0.02 M formed from **1** + MAO, Al/Ti = 50), almost complete decay of the imine ^{1}H NMR peaks of **3** was observed, followed by the appearance of the imine peak of the titanium-polymeryl species **4** at δ 8.10 ppm (cf. Figure 1e,f). Along with the intense line of the inner methylene groups of the growing polymeryl chains, three new peaks were found in the ^{13}C NMR spectra (Figure 3). Two of these, one at δ 23.4 (doublet, $^1J_{CC}$ = 34 Hz) and one at δ 32.6 (unresolved) belong to methylene carbons b and c of polyethenyl chain end groups (Scheme 2).[31d−e] The third signal at δ 111.5 ($\Delta\nu_{1/2}$ = 70 Hz) is assignable to a Ti-bound ^{13}CH$_2$-methylene group.[32] The Ti-^{13}CH$_2$− group in **4** thus experiences a significant downfield shift with respect to the Ti-^{13}CH$_3$ group in **3** (δ 87.2).[33] These results represent the first direct observation of Ti-bound polymeryl species in a living phenoxyimine titanium(IV)/MAO system.[34]

Conclusions

For the first time, cationic species formed from bis-[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (L$_2$TiCl$_2$) (**1**) by reaction with MAO or with AlMe$_3$/[CPh$_3$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ have been fully characterized by ^{1}H, ^{19}F, and ^{13}C NMR and EPR spectroscopy. From our results we can conclude that these reactions lead to the formation of outer sphere ion pairs [L$_2$TiMe(S)]$^+$[Me-MAO]$^-$ (**3**) and [L$_2$TiMe(S)]$^+$-[B(C$_6$F$_5$)$_4$]$^-$ (**3′**), respectively, with S being a weakly coordinated solvent molecule. In the absence of monomer, species **3** and **3′** are deactivated via transfer of the phenoxyimine ligand to aluminum under formation of LAlMe$_2$, and via reduction of Ti(IV) to Ti(III). Ion pairs **3** and **3′** react with ethylene to polymeryl species, which our results firmly establish to be [L$_2$TiP]$^+$[Me-MAO]$^-$ (**4**) and [L$_2$TiP]$^+$[B(C$_6$F$_5$)$_4$]$^-$(**4′**), with P being a growing polymeryl chain. These results thus represent the first unequivocal observation of Ti-bound polymeryl species in a living phenoxyimine titanium(IV)/MAO system.

Experimental Section

General Procedures. Methylaluminoxane (MAO) was purchased from Witco GmbH (Bergkamen, Germany) as a toluene solution (total Al content 1.8 M, Al as AlMe$_3$ 0.5 M). Ethylene-^{13}C$_2$ (99% ^{13}C) was purchased from Aldrich. Toluene-d_8 and 1,2-difluorobenzene were dried over molecular sieves (4 Å), degassed in vacuo, and stored under dry argon. Toluene was distilled over sodium or sodium-benzophenone under nitrogen and degassed in vacuo. All operations were carried out under dry argon by standard Schlenk techniques. Solids and toluene-d_8 were transferred and stored in a glovebox.

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(27) A signal at 7.9−8.0 ppm, reported by Makio and Fujita to arise upon addition of ethene, has been tentatively assigned by these authors to a thermally robust living polymeryl species.[13]

(28) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623.

(29) Carr, A. G.; Dawson, D. M.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1999**, *18*, 2933.

(30) The ^{19}F resonances of the phenoxyimine ligands were significantly broadened and thus uninformative.

(31) (a) Minott, R.; Fink, G.; Fenzl, W. *Angew. Makromol. Chem.* **1987**, *154*, 1. (b) Fink, G.; Fenzl, W. Minott, R. *Z. Naturforsch. B* **1985**, *40b*, 158. (c) Fink, G.; Rottler, R. *Angew. Makromol. Chem.* **1981**, *94*, 25. (d) Tritto, I.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1995**, *28*, 5358. (e) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1999**, *32*, 264.

(32) Terminal polymeryl methyl groups were not observable when the Ti-CH$_3$ groups of complex **3** were generated from L$_2$TiCl$_2$ and nonlabeled MAO.

(33) Similar downfield shifts of metal-CH$_2$ relative to metal-CH$_3$ groups have previously been reported in ^{13}C NMR studies on metallocene-based reaction systems.[31]

(34) After storing samples containing complex **4** at −20 °C, we observed partial chain transfer to aluminum.[35] After raising the temperature to −10 °C and storing the sample for several hours at this temperature, the Ti-^{13}CH$_2$ peak decayed completely. At room temperature, polymer chains released from aluminum clearly displayed terminal allyl signals, indicating substantial β-H elimination (see Supporting Information).

$[Ph_3C][B(C_6F_5)_4]$[36] and bis[*N*-3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride (**1**)[37] were prepared as described. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.130 and 75.473 MHz, respectively, on a Bruker Avance-300 MHz NMR spectrometer. Typical operating conditions for ^{13}C NMR measurements were as follows: spectral width 20 kHz; spectrum accumulation frequency 0.2−0.1 Hz; 100−2000 transients, 45° pulse at 5 μs. Multiplicities and coupling constants were derived from analysis of gated decoupled spectra. Operating conditions for ^{1}H NMR measurements: spectral width 5 kHz; spectrum accumulation frequency 0.5−0.2 Hz; number of transients 32−64, ca. 30° pulse at 2 μs. ^{13}C,^{1}H correlations were established by using standard Bruker HXCOBI pulse programs. For calculations of ^{1}H and ^{13}C chemical shifts, the resonances of the methyl group of the toluene-d_8 solvent were taken as 2.11 and 20.40 ppm, respectively. The ^{19}F chemical shifts were referenced to the chemical shift of 1,2-difluorobenzene (−139.0 ppm). The sample temperature measurement uncertainty and temperature reproducibility were less than ±1 °C.

Preparation of MAO and Al_2Me_6 Samples. Solid MAO was prepared from commercial MAO (Witko) by removal of the solvent in vacuo at 50 °C. The solid product obtained (polymeric MAO with total Al content 40 wt % and Al as residual $AlMe_3$ ca. 1−2 wt %) was used for the preparation of the samples. $^{13}CH_3$-enriched MAO was prepared by ligand exchange of 99% $^{13}CH_3$-enriched Al_2Me_6 (70 mol % of total Me groups) and solid MAO (30 mol % of total Me groups) in toluene solution followed by subsequent removal of volatiles under vacuum at room temperature to give a sample of ^{13}C-enriched MAO (65−70% ^{13}C) with desired Al_2Me_6 content (polymeric MAO with total Al content of 40% and Al as residual Al_2Me_6 ca. 5 wt %). A more detailed description is presented in ref 17.

Preparation of 1/MAO (+ethylene) Samples. The appropriate amounts of **1** and MAO were weighed in an NMR tube, and the tube was closed with septum stoppers. Further addition of toluene-d_8 was performed outside the glovebox with gastight microsyringes in the flow of nitrogen upon appropriate cooling. ^{1}H NMR (**3**, toluene-d_8/1,2-difluorobenzene, 20 °C): δ 8.32 (s, 2H, C*H*=N), 7.68 (d, 2H, Ar-*H*, J_{HH} = 7.5 Hz), 7.29 (d, 2H, Ar-*H*, J_{HH} = 7.5 Hz), 2.00 (s, 3H, Ti-C*H*$_3$), 1.40 (s, 18H, *t*Bu). ^{1}H NMR (**3**, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 8.81 (s, 1H, C*H*=N), 7.90 (s, 1H, C*H*=N), 1.95 (s, 3H, Ti-C*H*$_3$), 1.4 (br, *t*Bu).

Addition of ethylene or ethylene-$^{13}C_2$ (ethylene:Ti = 10, 20) to the above sample was performed with a gastight syringe by bubbling the gas through the cooled solution of **3**. The sample was placed in the NMR probe thermostated at −20 °C, and the NMR spectra of **4** were run at this temperature. ^{1}H NMR (**4**, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 8.10 (s, 2H, C*H*=N), 1.29 (s, 18H, *t*Bu).

Preparation 1/$AlMe_3$/$[Ph_3C]^+[B(C_6F_5)_4]^-$ (+ethylene) Samples. The appropriate amounts of **1** (typically, 0.045 mmol) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.049 mmol) were weighed in an NMR tube, and the tube was closed with septum stoppers. Further addition of Al_2Me_6 (2.0 M solution in toluene, Al/Ti= 10, 20, 25) was performed outside the glovebox with gastight microsyringes in a flow of nitrogen upon appropriate cooling. A brown oily phase precipitated in the bottom of the NMR tube. The upper (organic) phase containing toluene, Al_2Me_6, and Ph_3CMe was removed. The oily phase was washed with 1 mL of toluene, and after removal of toluene the oily phase was dissolved in toluene-d_8/1,2-difluorobenzene (9:1). ^{1}H NMR (**3′**, toluene-d_8/1,2-difluorobenzene, 20 °C): δ 8.38 (s, 2H, C*H*=N), 7.64 (d, 2H, Ar-*H*, J_{HH} = 8 Hz), 2.01 (s, 3H, Ti-C*H*$_3$), 1.35 (s, 18H, *t*Bu). ^{19}F NMR (**3′**, toluene-d_8/1,2-dichlorobenzene, 20 °C): δ −132.3 (2F, o-F), −163.2 (1F, p-F, J_{FF} = 20 Hz), −167.0 (2F, m-F). ^{19}F resonances due to the phenoxyimine ligands were broadened and therefore noninformative. ^{1}H NMR (**3′**, toluene-d_8/1,2-difluorobenzene, −20 °C): 8.76 (s, 1H, C*H*=N), 7.91 (s, 1H, C*H*=N), 2.00 (s, 3H, Ti-C*H*$_3$), 1.4 (br, *t*Bu).

Addition of ethylene ([ethylene]:[Ti] = 10, 20) to the above sample was performed with a gastight syringe by bubbling the gas through the cooled solution of **3′**. The sample was placed in a NMR probe thermostated at −20 °C, and the NMR spectra of **4′** were run at this temperature. ^{1}H NMR (**4′**, toluene-d_8/1,2-difluorobenzene, −20 °C): δ 8.10 (s, 2H, C*H*=N), 1.23 (s, 18H, *t*Bu).

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Supporting Information Available: ^{1}H NMR spectra of species **1**, **2**, and **3′** at different temperatures; ^{13}C NMR spectra of **4** at different temperatures and ^{13}C NMR spectrum of the resulting ^{13}C-polyethene. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Tritto et al. observed ^{13}C NMR peaks of α, β, and γ methylene carbons of the polymer chain bound to aluminum at 11.2, 25.8, and 36.4 ppm, respectively.[31e] The decay of ^{13}C-enriched polymeryl species **4** results in the appearance of ^{13}C NMR peaks at 12.6, 27.5, 35.2, and 38.9 ppm. This more complex picture may be the result of the presence of diverse Al-Me complexes in **1**/MAO systems, whereas in the Cp_2ZrMe_2/MAO system of Tritto et al., $AlMe_3$ is the only chain transfer agent. For ^{13}C NMR spectra see Supporting Information.

(36) Bochmann, M.; Lancaster, S, J. *J. Organomet. Chem.* **1992**, *434*, C1.

(37) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabary M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999**, 1263.